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## (54) Polymer composition

(57) A polymeric composition suitable for use as electrical insulation containing a tetraalkyl dialkoxydisiloxane as a water tree retardant additive. A particular example of the water tree retardant additive is tetramethyl dimethoxydisiloxane.

polymere + alkoxysilane + additifs
retarding growth of water tree.
Pas de charge.

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1982.

GB 2 210 045 A

# POLYMER COMPOSITION

The present invention relates to polymer compositions suitable for use in the field of wire and cable insulation and to a process for the production of such compositions. More particularly the invention relates to polymer compositions which exhibit an improved resistance to the initiation and growth of water trees when employed as medium and high voltage electrical insulation.

Polymer compositions suitable for use as insulating layers for electrical cables are well known. Generally, such compositions are based on polyolefins such as, for example, homopolymers and copolymers of ethylene. The polymer compositions may be used as insulation in an uncross-linked form, but preferably the compositions are cross-linked in order to provide improved high temperature properties.

When used as insulation for medium or high voltage power cable, polyolefins tend to undergo a phenomenon known as "treeing". the term "treeing" has been applied to this type of insulation breakdown because the failure path looks somewhat like the profile of a tree. Two types of "tree" have been identified and these are generally known as "electrical trees" and "water trees". It is generally believed that electrical trees are generated by corona discharges causing fusion and eventual breakdown of the polymer whereas water trees tend to occur in solid dielectric material which is simultaneously exposed to moisture and an electric field. Water treeing is therefore a significant factor in det rmining the useful life of buried medium and high voltage power cables. Water trees



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tend to be initiated at sites of high electrical stress such as rough interfaces, protruding conductive points, voids or embedded contaminants. Electrical trees and/or water trees can lead to electrical power leakage or even complete breakdown of the insulation.

A number of proposals for retarding the growth of water trees are suggested in the prior art. DT-A-2737430 describes an insulation composition having reduced tendency to form water trees comprising a polyolefin and an alkoxy silane. US-A-4299713 describes an unfilled polymeric composition for electrical insulation comprising a polymeric component and, as a water treeing and electrical treeing inhibitor for the composition, at least one defined organic compound which is a silicon, tin, titanium, phosphorus or boron compound for example, vinyl-tris-(2-methoxyethoxy) silane.

It is an object of the present invention to provide a polymeric composition suitable for use as electrical insulation having improved resistance to the initiation and/or growth of water trees.

Accordingly the present invention provides a composition suitable for use as electrical insulation comprising a polymeric component and a water tree retardant additive characterised in that the water tree retardant additive is a tetraalkyl dialkoxydisiloxane.

The present invention further provides a process for preparing a polymeric composition suitable for use as electrical insulation comprising mixing together a polymeric component and a water tree retardant additive characterised in that the water tree retardant additive is a tetraalky dialkoxydisiloxane.

The present invention also includes an electric wire or cable comprising an electrical conductor insulated by an insulation layer comprising a polymeric component and a water tree retardant additive characterised in that the water tree retardant additive is a tetraalkyl dialkoxydisiloxane.

The alkyl groups of the water tree growth retardant additive are preferably alkyl groups having from one to four carbon atoms. Preferably all four alkyl groups are th same. The alkoxy groups



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also preferably have from one to four carbon atoms. A particular example of a suitable water tree growth retardant additive for use in the present invention is tetramethyl dimethoxydisiloxane.

The quantity of water tree retardant additive in the composition of the present invention is suitably from 0.1 to 10%, preferably from 0.3 to 5% by weight, based on the combined weight of the polymeric component and the water tree retardant additive.

The polymeric component comprises a material suitable for use as an electrical insulating material and can be, for example, a homopolymer of ethylene or a copolymer comprising a major proportion of ethylene. The homopolymer or copolymer of ethylene can be, for example, low density polyethylene (LDPE); copolymers of ethylene with alkyl acrylate, copolymers of ethylene with alkyl methacrylate; copolymers of ethylene with vinyl acetate; linear ethylene polymers (e.g. HDPE) or linear ethylene copolymers (eg LLDPE). The polymeric component can also be a silyl polymer i.e. a polyolefin having incorporated therein hydrolysable silane groups which form crosslinks by hydrolysis and condensation in the presence of water and, preferably, a silanol condensation catalyst. Such silyl polymers can be prepared, for example, by copolymerising monomeric material such as ethylene with an unsaturated silane compound having hydrolysable groups, by grafting an unsaturated silane compound having hydrolysable groups on to a polymer such as a homopolymer or copolymer of ethylene or by transesterification with esters of silane compounds having hydrolysable groups of copolymers of ethylene with esters of unsaturated carboxylic acids (e.g. ethylene ethyl acrylate copolymers) or with vinyl acetate.

The polymeric component can comprise a blend of two or more of the above mentioned polymers. The polymeric component can comprise a blend of one or more of the above mentioned polymers with ethylene/propylene rubber (EPR) or ethylene/propylene/diene monomer (EPDM) rubber.

Particularly preferred as the polymeric component are LDPE, ethylene/methyl acrylate copolymer (EMA), ethylene/ethylacrylate copolymer (EEA), ethylene/butyl acrylate copolymer, ethylene/vinyl



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acetate copolymer (EVA) and linear low density polyethylene or blends of two or more thereof. Particularly preferred blends are LLDPE/LDPE, blends of EEA or ethylene/butyl acrylate copolymer with LDPE, LLDPE or LDPE/LLDPE and blends of EVA with LDPE, LLDPE or LDPE/LLDPE.

Preferably, the ethylene/alkylacrylate or ethylene/vinyl acetate copolymers, if used, contain from 1 to 30 weight% of copolymerised alkyl acrylate or vinyl acetate units based on the weight of the copolymer. A particularly preferred polymeric component comprises a blend of LDPE with ethylene/ethylacrylate copolymer wherein the total ethylacrylate content in the component lies in the range 0.5 to 5 wt%. The aforesaid polymers or blends can also contain other suitable insulating polymeric materials, for example, polypropylene. The melt index of the polymeric component (prior to any crosslinking) suitably lies in the range 0.1 to 10 as measured by ASTM D 1238 (2.16 Kg/190°C).

Silyl polymers are inherently cross-linkable in that they form crosslinks by hydrolysis and condensation in the presence of water and, preferably, a silanol condensation catalyst. Other polymeric compositions according to the present invention can contain a chemical crosslinking agent (e.g. an organic peroxide or hydroperoxide). Also, polymeric compositions according to the present invention can be crosslinked by the use of ionising radiation, subsequent to forming into useful articles if desired.

In one embodiment of the present invention a crosslinkable composition comprises the polymeric component, the water tree retardant additive and an organic peroxide or hydroperoxide crosslinking agent.

Examples of peroxide crosslinking agents suitable for use in this embodiment of the present invention are dicumyl peroxide, 2.5-bis(tertiary butyl peroxy)-2,5-dimethyl hexane, di-tertiary butyl peroxide, benzoyl peroxide, tertiary butyl cumyl peroxide, 2.5-bis(tertiary butyl peroxy)-2,5-dimethyl hexyne and bis (tertiary butyl peroxy) disopropyl benzene. The quantity of organic peroxide f r use in such crosslinkable compositions is suitably 0.3 to 10.0



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wt%, preferably 0.5 to 5.0 wt% based on the total composition. It will be understood that the peroxide is suitably selected so that it has a relatively long half life (eg greater than 0.5 hours) at the processing temperature but a relatively short half life (eg less than 10 minutes) at the temperature employed during the subsequent curing step.

In another embodiment of the present invention, a crosslinkable composition comprises, as the polymeric component, a silyl polymer the water tree retardant additive, and a silanol condensation catalyst.

Silyl polymers and their ability to be crosslinked in the presence of water and a silanol condensation catalyst are known in the art. For example, British Patent GB 2,028,831B discloses the preparation of a crosslinkable polyethylene resin composition comprising (A) a copolymer obtained by copolymerising ethylene monomer and a hydrolysable, ethylenically unsaturated silane monomer at elevated temperature and pressure in the presence of a radical initiator and (B) a silanol condensation catalyst. GB 2,039,513A discloses a process for producing insulated electrical conductors which process comprises extrusion coating an electrical conductor with such an ethylene/vinyl silane copolymer and thereafter subjecting the coated conductor to a crosslinking process step comprising causing the coated conductor to contact water in the presence of a silanol condensation catalyst. GB-A-1,357,549, GB-A-1,234,034 and GB-A-1,286,460 disclose silyl polymers produced by grafting a polyolefin with a hydrolysable, ethylenically unsaturated silane compound in the presence of a free radical initiator. A commercial example of a multi-extrusion process for producing silyl polymers by grafting is the SIOPLAS (registered trade mark) process and a commercial example of a single-extrusion process for producing silyl polymers by grafting is the MONOSIL (registered trade mark) process. When the silyl polymer is produced by grafting, the water tree growth retardant additive can be present in the component mixture during the grafting reaction. The "transesterification" method comprises treating a copolymer having



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exchangeable functions such as alkoxy groups (as, for example, in ethylene/ethyl acrylate copolymer) or carboxylate groups (as, for example, in ethylene/vinyl acetate copolymer) with a suitable silane compound in the presence of a special ester-exchange catalyst. A transesterification method is disclosed, for example, in US-A-4579913.

Preferably, when a silyl polymer is employed as the polymeric component in the composition of the present invention, it contains from 0.1 to 10 weight %, preferably from 0.5 to 5 weight % of copolymerised or grafted units of the unsaturated silane compound. Preferred hydrolysable, unsaturated silane compounds are vinyl trimethoxy silane, vinyl triethoxy silane and vinyl triacetoxy silane. The composition preferably also contains a silanol condensation catalyst, for example a dialkyl tin carboxylate such as dibutyl tin dilaurate or dibutyl tin maleate. The quantity of such catalyst is suitably 0.01 to 5%, preferably 0.03 to 3% by weight based on the quantity of silyl polymer.

The composition of the present invention can be prepared using techniques well known in the art to produce homogeneous dispersions of polymeric materials. The mixing is preferably carried out at a temperature such that the polymeric material is in the form of a melt. When the polymeric component is employed in the form of granules (e.g. pellets or powder) the mixing can be carried out, if desired, by contacting the granules with the water tree growth retardant, optionally with one or more other additives, e.g. antioxidant, under conditions which lead to absorption of the additives by the polymer. The components can be mixed, for example, using multi-roll mills, screw mills, continuous mixers, extruders, compounding extruders or Banbury mixers. Minor amounts of other additives, for example, antioxidant, plasticers or processing aids, metal deactivators, pigments, heat and light stabilizers and antistatic agents can be incorporated if desired.

The water tree retardant additive employed in the composition of the present invention exhibits good stability and ease of compounding compared with conventional water tree retardant



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compounds. They show little or no tendency to exude during thermoforming or to exude from thermoformed products, for example, from wire and cable insulation. The additive is non-staining.

The present invention is illustrated by the following Example and Comparative Test.

Example and Comparative Test

The following compositions intended for use as wire and cable insulation were homogenised using a two-roll mill and the products were compression moulded into plaques by heating the composition in a press finally at 190°C under a pressure of 25 bar for 15 minutes to cause crosslinking. The moulded plaques were then cooled to room temperature. The plaques were heated to 90°C in a vacuum oven (25 mm Hg pressure) to remove volatile materials before testing.

Composition A (Comparative)

A commercially available composition sold by BP Chemicals under the trade designation BPH-4201 comprising a blend of low density polyethylene, ethylene/ethyl acrylate copolymer, dicumyl peroxide (1.8 weight %) and a conventional antioxidant.

Composition B (Invention)

As composition A, except that the composition also contains 1.0% by weight (based on total composition) of tetra-methyl dimethoxydisiloxane.

The water tree growth rate (WTGR) of each of the plaques was determined using a test method similar to that described in European Patent Application EP-A-0023239.

A compression moulded dish-shaped specimen approximately 150mm in diameter was prepared for each composition. The geometry of the dish-shaped specimen was substantially as shown in EP 0023239. Four conical depressions were moulded into the bottom of the dish. 100ml of an electrolyte solution comprising a 0.01 N solution of sodium chloride was poured into the dish which was then placed into an earthed bath, containing the same electrolyte solution. A 50mm diameter platinum wire ring was then immersed in the electrolyte in the sample dish and connected to the voltage source. The temperature at which the test was carried out was 65°C, the



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frequency was 6KHz at 5 kV and the time for which test was carried out was 72 hours.

To measure the length of the water trees formed, the conical depressions were punched out using a circular die and an arbor press. The punched-out discs of specimens were placed in a boiling solution of 0.5g methylene blue and 8ml concentrated NaOH in 250ml of distilled water for 30 minutes. The discs were then sectioned and mounted on microscope slides for examination. The water tree growth rate was obtained by measuring the length of the water trees and calculating the rate constant for water treeing for each composition using the equations disclosed in EP 0023239. The rate constant (k) for each composition is given in the Table together with the relative water tree growth rate (WTGR) which is the ratio of the rate constant for the composition to the rate constant of a reference composition, in this case Composition A (i.e. k/kref.). The results clearly demonstrate the reduction in the water tree growth rate of the composition according to the present invention.

TABLE

| Composition | K ($mm^3/hr \times V^2$) | WTGR (k/k ref) |
|---|---|---|
| A | $3.252 \times 10^{-12}$ | 1.00 |
| B | $6.924 \times 10^{-13}$ | 0.21 |



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Claims:

1. A polymeric composition suitable for use as electrical insulation comprising a polymeric component and a water tree retardant additive characterised in that the water tree retardant additive is a tetraalkyl dialkoxydisiloxane.

2. A polymeric composition as claimed in claim 1 in which the alkyl groups of the water tree retardant additive have from one to four carbon atoms.

3. A polymeric composition as claimed in claim 1 or claim 2 in which all four alkyl groups are the same.

4. A polymeric composition as claimed in any one of claims 1 to 3 in which the alkoxy groups of the water tree retardant have from one to four carbon atoms.

5. A polymeric composition as claimed in claim 1 in which the water tree retardant is tetramethyl dimethoxydisiloxane.

6. A polymeric composition as claimed in any one of claims 1 to 5 in which the amount of water tree retardant in the composition is from 0.1 to 10% by weight, based on the combined weight of the polymeric component and the water tree retardant additive.

7. A polymeric composition according to claim 1, substantially as described in the Example.

8. A process for preparing a polymeric composition suitable for use as electrical insulation comprising mixing together a polymeric component and a water tree retardant additive characterised in that the water tree retardant additive is a tetraalkyl dialkoxydisiloxane.

9. A process as claimed in claim 8 in which the water tree retardant is tetramethyl dimethoxydisiloxane.

10. An electric wire or cable comprising an electrical conductor insulated by an insulation layer comprising a polymeric component as claimed in any one of claims 1 to 7.

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